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TRANSLATION

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L9: Entry 1 of 1

File: DWPI

Jun 22, 1999

DERWENT-ACC-NO: 1999-414534

DERWENT-WEEK: 199938

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TITLE: Explosion protection valve gear for lithium secondary battery - has washer threaded to rivet which electrically connects lead board and rivet through insulation gasket

PATENT-ASSIGNEE:

ASSIGNEE

MATSUSHITA DENKI SANGYO KK

CODE

MATU

PRIORITY-DATA: 1997JP-0332632 (December 3, 1997)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP <u>11167909</u> A	June 22, 1999		009	H01M002/12

APPLICATION-DATA:

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JP 11167909A	December 3, 1997	1997JP-0332632	

INT-CL (IPC): H01 M 2/04; H01 M 2/08; H01 M 2/12; H01 M 10/40

ABSTRACTED-PUB-NO: JP 11167909A

BASIC-ABSTRACT:

NOVELTY - A rivet (5) functioning as terminal is arranged in the sealing board (2) and a metal washer (7) is threaded on the rivet, to electrically connect the lead board (13) and rivet through lower insulation gasket (8). The insulation gasket (6) insulates the sealing board from the rivet. DETAILED DESCRIPTION - The hole (4) provided in the sealing board, is sealed by an explosion protection valve (3) and a resin film covers the lower portion of the hole.

USE - For lithium secondary battery used as power supply in PC, AV apparatus.

ADVANTAGE - Explosion protection valve gear has high safety, high dependability and excels in leak resistance, since gas is ejected accurately. DESCRIPTION OF DRAWING(S) - The figure shows principal part cross sectional view of explosion protection valve gear. (2) Sealing board; (3) Explosion protection valve; (4) Hole; (5) Rivet; (6,8) Insulation gaskets; (7) Metal washer; (13) Lead board.

CHOSEN-DRAWING: Dwg.1/4

TITLE-TERMS: EXPLOSIVE PROTECT VALVE GEAR LITHIUM SECONDARY BATTERY WASHER THREAD RIVET ELECTRIC CONNECT LEAD BOARD RIVET THROUGH INSULATE GASKET

DERWENT-CLASS: X16

EPI-CODES: X16-B01F1; X16-F01; X16-F01A; X16-F03B;

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L4: Entry 5 of 7

File: DWPI

Jun 22, 1999

DERWENT-ACC-NO: 1999-414534

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CHOSEN-DRAWING: Dwg.1/4

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DERWENT-CLASS: X16

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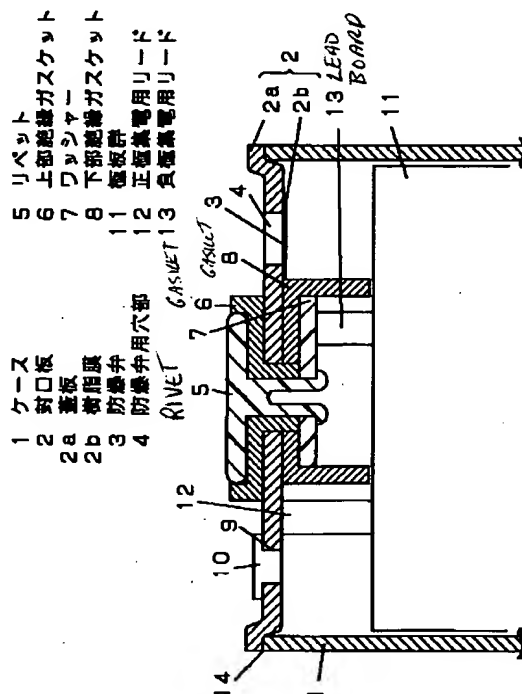
(74) 代理人 弁理士 滝本 智之 (外1名)

(54) 【発明の名称】 非水電解液電池用防爆弁装置

(57) 【要約】

【課題】 電池の誤使用や異常事態等での電池内圧の上昇に対して精度良くガスを排出することができ、かつ耐漏液性に優れた高い安全性と信頼性を有する防爆弁装置を提供することを目的とする。

【解決手段】 ケース1の開孔部を封口し、防爆弁用穴部4に樹脂膜2bを溶着した封口板2と、封口板2の中央部に挿入された端子を兼ねるリベット5と、封口板2とリベット5を絶縁する樹脂製の上部絶縁ガスケット6を備え、リベット5の下部絶縁ガスケット8を介してリベット5と極板群11の同極性のリード板とを電気的に接続する金属製のワッシャー7を備え非水電解液電池用防爆弁装置とする。



## 【特許請求の範囲】

【請求項1】 極板群と電解液を内部に収容するケースと、前記ケースの開口部を封口し防爆弁を備えた封口板と、前記封口板に配設された端子を兼ねるリベットと、前記封口板と前記リベットを絶縁する樹脂製の上部絶縁ガスケットと、前記リベットの下部は樹脂製の下部絶縁ガスケットを介して前記リベットと同極性のリード板とを電氣的に接続する金属製のワッシャーを備えており、前記封口板は、蓋板に防爆弁用穴部が設けられており、前記防爆弁用穴部の下部を樹脂膜で覆うことにより構成した非水電解液電池用防爆弁装置。

【請求項2】 上部絶縁ガスケットは、ペルフルオロアルコキシフッ素樹脂、ポリサルホン樹脂、ポリフェニレンスルフィド樹脂のなかから選ばれた材質である請求項1記載の非水電解液電池用防爆弁装置。

【請求項3】 下部絶縁ガスケットは、ペルフルオロアルコキシフッ素樹脂、ポリサルホン樹脂、ポリフェニレンスルフィド樹脂のなかから選ばれた材質である請求項1記載の非水電解液電池用防爆弁装置。

【請求項4】 下部絶縁ガスケットは、極板群の集電用リードと電氣的に接続する金属製のワッシャーを囲むように極板群の方向に折れ曲がった形状をしている請求項1記載の非水電解液電池用防爆弁装置。

【請求項5】 防爆弁用穴部の下部に配設された樹脂膜は、ポリエチレンテレフタレート樹脂、ペルフルオロアルコキシフッ素樹脂、ポリサルホン樹脂、ポリフェニレンスルフィド樹脂のなかから選ばれた1種類の材質である請求項1記載の非水電解液電池用防爆弁装置。

【請求項6】 防爆弁用穴部の下部に配設された樹脂膜は、10～100 $\mu$ mの厚さで構成されており、2～15kgf/cm<sup>2</sup>の加圧により破断するようにした請求項1記載の非水電解液電池用防爆弁装置。

【請求項7】 封口板の防爆弁は、蓋板に設けられた防爆弁用穴部の下部のみをアルミニウム箔で覆うか、あるいは蓋板の下面全体をアルミニウム箔で覆うことにより構成されていて、前記アルミニウム箔は、10～40 $\mu$ mの厚さで構成されており、2～15kgf/cm<sup>2</sup>の加圧により破断するようにした請求項1記載の非水電解液電池用防爆弁装置。

【請求項8】 封口板の防爆弁は、蓋板に設けられた防爆弁用穴部の下部のみを超音波溶着にてアルミニウム箔で覆うか、あるいは蓋板の下面全体を超音波溶着にてアルミニウム箔で覆うことにより構成されていて、前記アルミニウム箔は、10～40 $\mu$ mの厚さで構成されており、2～15kgf/cm<sup>2</sup>の加圧により破断するようにした請求項1記載の非水電解液電池用防爆弁装置。

【請求項9】 封口板の防爆弁用穴部の上面に、前記防爆弁用穴部の中心方向に突出する針状突起部を有するように防爆弁用穴部上面を変形させた請求項1記載の非水電解液電池用防爆弁装置。

【請求項10】 封口板の防爆弁用穴部の上面に、前記防爆弁用穴部の下面方向に針状突起部を有する金属板を溶接した請求項1記載の非水電解液電池用防爆弁装置。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、薄型の非水電解液電池の、特にその封口板の防爆弁装置に関するものである。

【0002】

【従来の技術】近年、通信機、AV機器、パソコンのコードレス化、ポータブル化に伴いその駆動用電源である電池に対して小型、軽量、高エネルギー密度化の要望が強まっている。特にリチウム二次電池は高エネルギー密度を有する電池であり次世代の主力電池として期待され、その潜在的市場規模も大きい。また、形状としては機器の薄型化あるいは機器のスペースの有効利用の観点からも角形電池の要望が高まっている。

【0003】しかし、リチウム二次電池は短絡、過充電、逆充電等の電池の誤使用や、異常事態において電解液や活物質の分解により電池内でガスが発生し、蓄積されて電池内圧が急激に上昇することにより破裂や発火する可能性があった。

【0004】このような電池の急激な内圧上昇を未然に防止するために、特開平2-112151号公報に示されたように内圧の上昇に伴い変形する防爆弁が備えられており、電池内圧値が所定の値に達した時、防爆弁が破断して電池内に蓄積されたガスを電池外に放出する防爆弁装置が知られている。

【0005】

【発明が解決しようとする課題】しかしながら、前記のような防爆弁装置を備えた電池は、複雑な電流遮断機構あるいは防爆構造を備えており、その構造が複雑であるため製造工程に数々の検査工程を具備しなければならず信頼性の高い防爆弁装置を得ることは困難であった。

【0006】本発明は、前記従来例に比較して高い信頼性を有する防爆弁装置を提供するものである。

【0007】

【課題を解決するための手段】本発明の構成は、極板群と電解液を内部に収納するケースと、前記ケースの開口部を封口し防爆弁を備えた封口板と、前記封口板に配設された端子を兼ねるリベットと、前記封口板と前記リベットを絶縁する樹脂製の上部絶縁ガスケットと、前記リベットの下部は樹脂製の下部絶縁ガスケットを介して前記リベットと同極性のリード板とを電氣的に接続する金属製のワッシャーを備えており、前記封口板は、蓋板に防爆弁用穴部が設けられており、前記防爆弁用穴部の下部をポリプロピレン樹脂膜で覆うように構成されている。

【0008】これにより、短絡、過充電、逆充電等の電池の誤使用や、異常事態における電池内圧の上昇に対し

て、封口板に設けられた防爆弁のポリプロピレン樹脂膜が破断し、電池内のガスを排出することにより電池の急激な温度上昇や電池内圧の上昇を効果的に防止することが可能となる。なお、防爆弁である樹脂膜の材質としては、ポリプロピレンの他にポリエチレンテレフタレート樹脂、ペルフルオロアルコキシフッ素樹脂、ポリサルホン樹脂から選ばれた1種類が好適である。

【0009】また、樹脂膜の厚みは、10～100 $\mu$ mが好適であり、樹脂膜の破断する圧力は、2～15kgf/cm<sup>2</sup>に設定することで、より効果的に電池の急激な温度上昇や電池内圧の上昇を防止することができる。

【0010】また、防爆弁用穴部の上面には防爆弁用穴部の中心方向に突出する針状突起部を有するように防爆弁用穴部上面を変形させるか、あるいは防爆弁用穴部の下面方向に針状突起部を有する金属板を溶接すると、より安定した樹脂膜の破断する圧力が得られる。

【0011】また、前記封口板の防爆弁は、蓋板に設けられた防爆弁用穴部の下部にアルミニウム箔を溶着するか、あるいは蓋板の下面全体にアルミニウム箔を溶着する構成とすることにより、短絡、過充電、逆充電等の電池の誤使用や、異常事態における電池内圧の上昇に対して、封口板に設けられた防爆弁のアルミニウム箔が破断し、電池内のガスを排出することにより電池の急激な温度上昇や電池内圧の上昇を効果的に防止することが可能となる。その際、前記アルミニウム箔は、10～40 $\mu$ mの厚さが好適であり、アルミニウム箔の破断する圧力は2～15kgf/cm<sup>2</sup>に設定することで、より効果的に電池の急激な温度上昇や電池内圧の上昇を防止することができる。

【0012】また、防爆弁用穴部の上面には防爆弁用穴部の中心方向に突出する針状突起部を有するように防爆弁用穴部上面を変形させるか、あるいは防爆弁用穴部の下面方向に針状突起部を有する金属板を溶接した場合は、より安定した樹脂膜を破断する圧力が得られる。

【0013】また、封口板の上部絶縁ガスケットおよび下部絶縁ガスケットは、耐熱性に優れ、かつ耐電解液性に優れたポリエチレンテレフタレート樹脂、ペルフルオロアルコキシフッ素樹脂、ポリサルホン樹脂、ポリフェニレンスルフィド樹脂から選ばれた1種類の材質でそれぞれ成形した場合は、それらを組み合わせることで耐漏液性に優れ信頼性の高い封口板が得られる。また下部絶縁ガスケットは、極板群のリード板とを電氣的に接続する金属製のワッシャーを囲むように極板群の方向に折れ曲がった形状にした場合には、ワッシャーと極板群との接触を防止し、安全性の高い電池が得られる。

【0014】

【発明の実施の形態】本発明の非水電解液電池用防爆弁装置では、極板群と電解液を内部に収納するケースと、前記ケースの開口部を封口し、防爆弁用穴部に樹脂膜を溶着した封口板と、封口板の中央部に挿入された端子を

兼ねるリベットと、封口板とリベットを絶縁する上部絶縁ガスケットと、リベットの下部絶縁ガスケットを介してリベットと極板群の同極性のリード板とを電氣的に接続する金属製のワッシャーを備えており、ケースと封口板は、レーザ溶接によって溶着することができ、封口板に注液口を設けたもの、封口板の周縁部が凹状にへこんだもの、防爆弁用穴部が円形であるもの、防爆弁用穴部の上面に防爆弁用穴部の中心方向に突出する針状突起部を有するように防爆弁用穴部上面を変形させたもの、あるいは防爆弁用穴部の上面に、防爆弁用穴部の下面方向に針状の突出部を有する金属板を溶接しているもの、また、封口板の蓋板の防爆弁用穴部の下部あるいは蓋板の下面全体をアルミニウム箔で覆うか超音波溶着によりアルミニウム箔が溶着されているものを実施形態とすることができる。

【0015】

【実施例】以下、本発明の具体的な実施例を図面を参照しながら説明する。

【0016】図1は、本発明の非水電解液電池用防爆弁装置を装着した電池の断面図の一例である。1はアルミニウム製の角形のケースである。2は封口板で、アルミニウム製の平板状の蓋板2aに防爆弁3が設けられている。そして、防爆弁3は蓋板2aの防爆弁用穴部4の下面がポリプロピレン製の樹脂膜2bで覆われている。この封口板2は角形のケース1とレーザ溶接されている。5はニッケルメッキされた鉄製の端子を兼ね、封口板2の中央部に配設されたリベット、6は封口板2とリベット5を絶縁する上部絶縁ガスケット、7はニッケルメッキされた鉄製のワッシャー、8は封口板2とワッシャー7を絶縁する下部絶縁ガスケットである。このリベット5は封口板2の中央部の開口部に上部絶縁ガスケット6を介して挿入され、リベット5の下部に下部絶縁ガスケット8を介してワッシャー7を配設した後、リベット5をかしめることによりリベット5とワッシャー7の電氣的接続をとるとともに、蓋板2aとの絶縁も確保している。9は蓋板2aに開けられた注液口で、10は注液口9を塞ぐ栓である。11は正極板、負極板をセパレータを介して巻回し、長円形にプレス圧縮された極板群である。12は正極板から取り出したアルミニウム製の正極集電用リードで蓋板2aに溶接されている。また、13は負極板から取り出したニッケル製の負極集電用リードでワッシャー7に溶接されている。従って、電池としてはケース1が正極で、リベット5からなる端子が負極となる。そして、この封口板2では、電池の短絡、過充電、逆充電等の異常使用時における電池内のガスの蓄積による電池内圧が上昇した際には、封口板2に設けられた防爆弁用穴部4のポリプロピレンの樹脂膜2bが破断され、電池内のガスを排出することにより、電池内圧の急激な上昇を防止することが可能となる。

【0017】本発明の非水電解液電池用防爆弁装置を装

着した電池は、以下のようにして作製した。正極板は、活物質である $\text{LiCoO}_2$ に導電剤としてカーボンブラックを、結着剤としてポリ四フッ化エチレンの水性ディスパーションを固形分の重量比で100:3:10の割合で混合したものをアルミニウム箔の両面に塗着、乾燥し、圧延した後、所定の大きさに切断した。これにアルミニウム製の正極集電用リード板を溶接している。負極板は、炭素質材料を主材料とし、これとスチレンブタジエンゴム系結着剤とを重量比で100:5の割合で混合したものを銅箔の両面に塗着、乾燥し、圧延した後、所定の大きさに切断した。これにニッケル製の負極集電用リードを溶接している。セパレータは、ポリエチレン製の微多孔フィルムである。正極板、負極板をセパレータを介して巻回し、上面が長円形の極板群とする。

【0018】極板集電用リード13を封口板2に溶接し角形のケース1に挿入し、封口板2とケース1をレーザ溶接により封口する。図1に示したように正極集電用リード12はアルミニウム製の封口板2の蓋板2aにレーザスポット溶接し、負極集電用リード13はニッケルメッキされた鉄製のワッシャー7に抵抗溶接した。次に、電解液を注液口9から所定量注液する。本実施例では、注液口9の先端にゴム製のリングが取り付けられているパイプを差し込む。パイプは、3方コックが備えてあり、一方は電池に、一方は真空ポンプに、もう一方は電解液が入ったポンプに接続されている。

【0019】パイプを通して電池内を真空ポンプで減圧に引く。次に、コックを切り替え電解液をポンプから注入する方法で注液を行った。一度電池内を減圧に引くことで電解液の注入が容易になる。電解液には、エチレン

カーボネートとジエチルカーボネートをモル比で1:3で混合した溶媒に溶質として六フッ化リン酸リチウムを1モル/リットルの濃度で溶解したものをを用いた。

【0020】(実施例1) 封口板2とリベット5を絶縁する上部絶縁ガスケット6および封口板2とワッシャー7を絶縁する下部絶縁ガスケット8について説明する。樹脂材料としては、一般にポリプロピレン樹脂が非水電解液電池で使用されている。この樹脂は成形性が良くコストも低いいためコイン型リチウム電池等で広く用いられているが、高温耐熱性に課題を有している。本発明の封口板2は、ケース1とレーザ溶接部14でレーザ溶接するため樹脂への熱影響が懸念され熱的に比較的安定な樹脂であることが望まれる。本実施例では、耐有機溶剤性や耐熱性等の既存データを参照にポリプロピレン(以下、PPという)、ペルフルオロアルコキシフッ素樹脂(以下、PFAという)、ポリサルホン樹脂(以下、PSという)、ポリフェニレンスルフィド樹脂(以下、PPSという)の4種類に絞り込み、それぞれを上部絶縁ガスケット6と下部絶縁ガスケット8に組み合わせて評価した。これらの樹脂を用いて封口板2および電池を作製し、高温保存時の電池漏液試験を行うことで樹脂の選定を行った。表1に各電池(各 $n=100$ セル)の漏液率を示した。なお、漏液試験方法は $-50^\circ\text{C}$ で1時間保存した後、 $100^\circ\text{C}$ で1時間保存する工程を1サイクルとして1000サイクル後の電池漏液品の数をカウントした。

【0021】

【表1】

樹脂材料		漏液率(%)
上部絶縁ガスケット	下部絶縁ガスケット	
PP	PP	70%
PFA	PP	10%
PP	PPS	40%
PFA	PFA	0%
PS	PS	0%
PPS	PPS	0%
PFA	PPS	0%
PPS	PS	0%
PS	PFA	0%

【0022】表1に示したように本発明のような封口板構造においては、従来使用されていたPPに対して、PFA、PS、PPSを用いることで飛躍的に耐漏液性が向上する。また、PFA、PS、PPSを表1以外に任意に組み合わせても耐漏液性を確保できる。

【0023】（実施例2）封口板2の防爆弁用穴部4の上面に、穴部の下面方向に針状突起部15を設ける利点について説明する。本発明では封口板2の蓋板2aに防爆弁用穴部4を設け、その下面をPP膜で覆う防爆弁構造をしているが、電池内圧が異常に上昇し、防爆弁3が作動する時にはPP膜が上方に膨らみ、その後、破断する。従って、PP膜の厚みや防爆弁用穴部4の形状等に\*

\*より、弁作動圧が大きく影響される。

【0024】本発明では、図2に示したように防爆弁用穴部4の上面に、前記防爆弁用穴部4の下面方向に針状突起部15を有する金属板16を溶接することにより防爆弁作動時に防爆弁3の破断位置を限定し作動圧の安定化を図ることができる。このような防爆弁用穴部4の上面に、針状突起部15を設けた場合と設けない場合での作動圧のバラツキの比較を行った。その結果を表2に示した。

【0025】

【表2】

針状突起部の有無	弁作動圧平均[kgf/cm <sup>2</sup> ]	バラツキ[σ]
有り	9.8	0.4
無し	10.1	0.9

【0026】表2より明らかなように針状突起部15を設けたほうがバラツキが少なく安定する。また、本実施例では針状突起部15を有する金属板16を溶接したが、図3に示したように封口板2の蓋板2a上面の一部を変形させて針状突起部15を設けても良い。

【0027】（実施例3）封口板2の防爆弁3の弁作動圧について図4を用いて説明する。防爆弁3は通常の電※

※池使用時には、電池の密閉性を有し、電池の異常使用時における電池内圧の急激な上昇時には、確実に弁作動し電池内のガスを外部に放出する、そのために適正な作動圧を設定する必要がある。本実施例においては、防爆弁3としてPP膜および超音波溶接したアルミニウム箔2cを用いて弁作動圧の評価を行った。また、前記防爆弁3を備えた電池を作製し電池漏液試験と過充電安全性評

価を行った。表3に弁作動圧の評価結果を、また表4に電池漏液試験および過充電安全性試験結果を示した。なお、漏液試験方法は-50℃で1時間保存した後、100℃で1時間保存する工程を1サイクルとして1000サイクル後の電池漏液品の数をカウントした。また、過\*

\* 充電安全性試験方法は満充電状態の電池をさらに無制御2C充電した時の電池発火の有無を確認した。

【0028】

【表3】

		弁作動圧平均[kgf/cm <sup>2</sup> ]	バラツキ[σ]
PP膜 (膜厚み)	8μm	1.2	1.1
	10μm	3.7	0.5
	60μm	9.8	0.4
	100μm	13.5	0.4
	120μm	20.7	0.8
アルミニウム箔膜 (膜厚み)	8μm	1.0	1.0
	10μm	3.0	0.3
	40μm	13.1	0.4
	50μm	17.3	1.9

【0029】

※30※【表4】



		漏液率(%)	安全性(発火の有無)
PP膜 (膜厚み)	8 $\mu$ m	45%	発火なし
	10 $\mu$ m	0%	発火なし
	60 $\mu$ m	0%	発火なし
	100 $\mu$ m	0%	発火なし
	120 $\mu$ m	0%	発火
アルミニウム箔膜 (膜厚み)	8 $\mu$ m	50%	発火なし
	10 $\mu$ m	0%	発火なし
	40 $\mu$ m	0%	発火なし
	50 $\mu$ m	0%	発火

【0030】表4よりPP膜、アルミニウム箔膜ともに、10 $\mu$ m以下の厚みでは電池の漏液が発生している。これは電池内の微量水分の分解や電解液の分解等によるガス発生により弁作動したと考えられる。また、PP膜100 $\mu$ m以上や、アルミニウム箔膜40 $\mu$ m以上では弁作動よりもレーザ溶接部14が先に開放し発火したと考えられる。上記結果と表3より、作動圧2~15 kgf/cm<sup>2</sup>が防爆弁の適正な作動圧である。

【0031】また、本実施例ではPP膜、アルミニウム箔膜を用いたが、ポリエチレンテレフタレート樹脂膜、PFA膜、PS膜、PPS膜でも良い。

【0032】(実施例4) 封口板2の下部絶縁ガスケット8が図1に示したように極板群11の方向に折れ曲がった形状をしている利点について説明する。本発明では下部絶縁ガスケット8を介してワッシャー7を配設しリベット5でかしめる構造であり、前記ワッシャー7には極板群11の負極集電用リード13が溶接されている。従って、電池の落下衝撃時、特に逆さ向けに落下した場合等では極板群11が電池上方にズレ上がり負極集電用\*

\*リード13が折れ曲がって極板群11に食い込んだり、ケース1と接触したりして内部ショートを引き起こす可能性がある。それに対して極板群11と封口板2の間に下部絶縁ガスケット8を配設することにより極板群11のズレ上りを抑制し、電池の安全性を確保できると考えられる。

【0033】本発明では、図1に示したように下部絶縁ガスケット8が極板の負極集電用リード13と電氣的に接続する金属製のワッシャー7を囲むように極板群11の方向に折れ曲がった形状をしていることで落下衝撃時等において極板のズレ上りを抑制している。このような下部絶縁ガスケット8の折れ曲がり部を設けた場合と設けない場合で電池の落下衝撃試験を行い、結果を表5に示した。なお、電池の落下衝撃試験方法は、電池を逆さまにして高さ1mからコンクリート上に20回落下した時の電池の内部ショート発生数をカウントした。

【0034】

【表5】

下部絶縁ガスケット 折れ曲がり部の有無	内部ショート発生率(%)
有り	0%
無し	60%

【0035】表5より明らかなように下部絶縁ガスケット※50※トの折れ曲がり部を設けたほうが電池の信頼性を向上す

ることができる。

【0036】

【発明の効果】以上のように本発明によれば、短絡、過充電、逆充電等の電池の誤使用や異常事態等での電池内圧の上昇に対して精度良くガスを排出することができ、かつ耐漏液性に優れた高い安全性と信頼性を有する非水電解液電池用の防爆弁装置を提供することができる。

【図面の簡単な説明】

【図1】本発明の実施例1、4における防爆弁装置の要部縦断面図

【図2】同実施例2における防爆弁装置の要部縦断面図

【図3】同実施例2における防爆弁装置の他の例を示す要部縦断面図

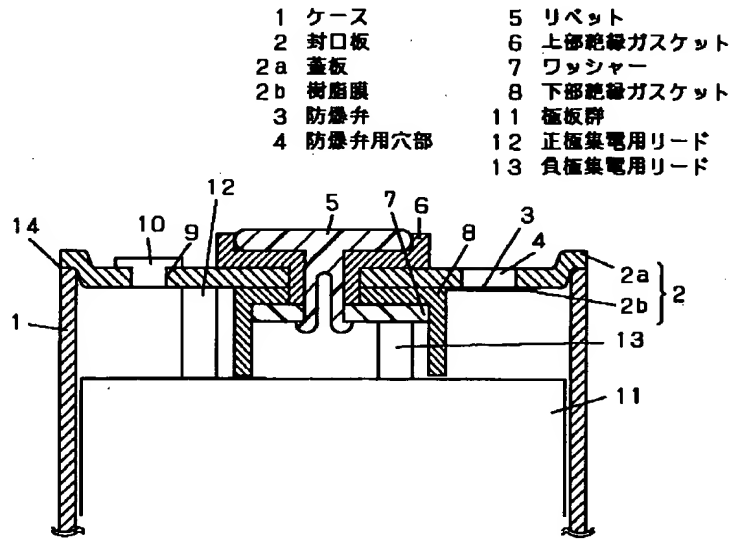
【図4】同実施例3における防爆弁装置の要部縦断面図

【符号の説明】

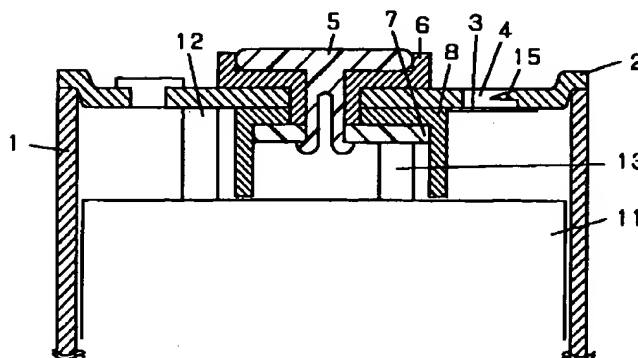
- 1 ケース
- 2 封口板

- 2a 蓋板
- 2b 樹脂膜
- 2c アルミニウム箔
- 3 防爆弁
- 4 防爆弁用穴部
- 5 リベット
- 6 上部絶縁ガスケット
- 7 ワッシャー
- 8 下部絶縁ガスケット
- 10 注液口
- 10 栓
- 11 極板群
- 12 正極集電用リード
- 13 負極集電用リード
- 14 レーザ溶接部
- 15 針状突起部
- 16 金属板

【図1】

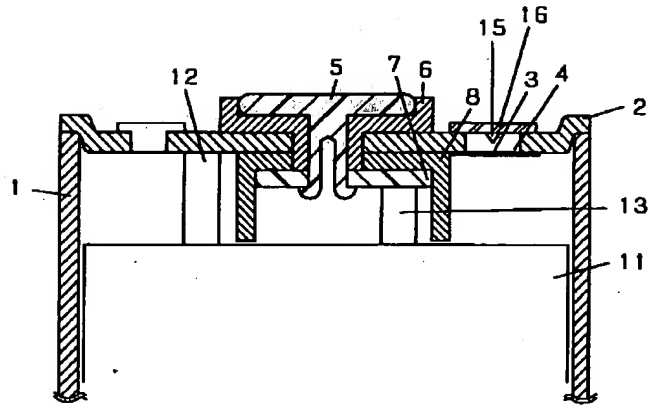


【図3】



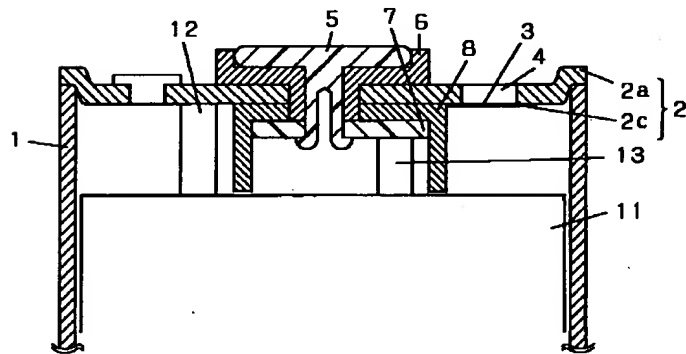
【図2】

15 針状突起部  
16 金属板



【図4】

2c アルミニウム箔



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is the thing of a thin nonaqueous electrolyte cell concerning the explosion-proof valve gear of the obturation board especially.

[0002]

[Description of the Prior Art] In recent years, the request of small, lightweight, and the formation of high-energy density has become strong to the cell which is the power supply for a drive with cordless-izing of a transmitter, an AV equipment, and a personal computer, and portable-izing. Especially a lithium secondary battery is a cell which has high-energy density, and is expected as a prime cell of the next generation, and the potential market size is also large. Moreover, as a configuration, the requests of a square shape cell are mounting also from a viewpoint of a deployment of thin-shape-izing of a device, or the space of a device.

[0003] However, in the misuse of cells, such as a short circuit, overcharge, and reverse charge, and the unusual situation, gas may have occurred within the cell by decomposition of the electrolytic solution or an active material, and the lithium secondary battery may have exploded and ignited, when it was accumulated and cell internal pressure rose rapidly.

[0004] In order to prevent rapid internal pressure elevation of such a cell beforehand, as shown in JP,2-112151,A, it has the explosion-proof valve deformed with elevation of internal pressure, and when a cell internal pressure value reaches a predetermined value, the explosion-proof valve gear which emits the gas which the explosion-proof valve fractured and was accumulated in the cell out of a cell is known.

[0005]

[Problem(s) to be Solved by the Invention] However, the cell equipped with the above explosion-proof valve gears was difficult for having a complicated current breaker style or a complicated explosion-proof construction, having to provide many inspection processes in a manufacturing process, since the structure is complicated, and obtaining a reliable explosion-proof valve gear.

[0006] this invention offers the explosion-proof valve gear which has high reliability as compared with the aforementioned conventional example.

[0007]

[Means for Solving the Problem] The obturation board which the composition of this invention obturated opening of a group of electrode, the case which contains the electrolytic solution inside, and the aforementioned case, and was equipped with the explosion-proof valve, The up insulating gasket made of a resin which insulates the rivet which serves as the terminal arranged by the aforementioned obturation board, and the aforementioned obturation board and the aforementioned rivet, The lower part of the aforementioned rivet is equipped with the metal washer which connects electrically the aforementioned rivet and the lead board of like-pole nature through the lower insulating gasket made of a resin. the aforementioned obturation board The hole for explosion-proof valves is prepared in the cover plate, and it is constituted so that the lower part of the aforementioned hole for explosion-proof valves may be covered by the polypropylene resin film.

[0008] The polypropylene resin film of the explosion-proof valve prepared in the obturation board fractures by this to the misuse of cells, such as a short circuit, overcharge, and reverse charge, and elevation of the cell internal pressure in the unusual situation, and it becomes possible by discharging the gas in a cell to prevent effectively a temperature rise and elevation of cell internal pressure with a rapid cell. In addition, as the quality of the material of the resin film which is an explosion-proof valve, one kind chosen from a polyethylene-terephthalate resin, a perfluoro-alkoxy fluororesin, and polysulphone resin besides polypropylene is suitable.

[0009] Moreover, the pressure which 10-100 micrometers is suitable for the thickness of a resin film, and a resin film fractures is 2 - 15 kgf/cm<sup>2</sup>. By setting up, a temperature rise and elevation of cell internal pressure with a rapid cell can be prevented more effectively.

[0010] Moreover, welding of the metal plate which is made to deform the hole upper surface for explosion-proof valves into the upper surface of the hole for explosion-proof valves so that it may have the needlelike height which projects in the direction of a center of the hole for explosion-proof valves, or has a needlelike height in the direction of an inferior surface of tongue of the hole for explosion-proof valves obtains the pressure which the resin film stabilized more fractures.

[0011] The explosion-proof valve of the aforementioned obturation board moreover, by considering as the composition which welds [ of the hole for explosion-proof valves prepared in the cover plate ] an aluminum foil, or welds [ of a cover plate /

whole ] an aluminum foil The aluminum foil of the explosion-proof valve prepared in the obturation board fractures to the misuse of cells, such as a short circuit, overcharge, and reverse charge, and elevation of the cell internal pressure in the unusual situation, and it becomes possible by discharging the gas in a cell to prevent effectively a temperature rise and elevation of cell internal pressure with a rapid cell. The pressure which the thickness of 10-40 micrometers is suitable for the aforementioned aluminum foil, and an aluminum foil fractures is 2 - 15 kgf/cm<sup>2</sup> in that case. By setting up, a temperature rise and elevation of cell internal pressure with a rapid cell can be prevented more effectively.

[0012] Moreover, when the metal plate which is made to deform the hole upper surface for explosion-proof valves into the upper surface of the hole for explosion-proof valves so that it may have the needlelike height which projects in the direction of a center of the hole for explosion-proof valves, or has a needlelike height in the direction of an inferior surface of tongue of the hole for explosion-proof valves is welded, the pressure which fractures the resin film stabilized more is obtained.

[0013] Moreover, when it fabricates with one kind of quality of the material chosen from the polyethylene-terephthalate resin which excelled [ insulating gasket / the up insulating gasket and lower insulating gasket / of an obturation board ] in thermal resistance, and was excellent in electrolytic-solution-proof nature, a perfluoro-alkoxy fluororesin, polysulphone resin, and the polyphenylene-sulfide resin, respectively, it excels in combining them at liquid spill-proof nature, and a reliable obturation board is obtained. Moreover, when a lower insulating gasket is made into the configuration which bent in the direction of a group of electrode so that the metal washer which connects the lead board of a group of electrode electrically may be surrounded, contact to a washer and a group of electrode is prevented, and the high cell of safety is obtained.

[0014]

[Embodiments of the Invention] The case which contains a group of electrode and the electrolytic solution inside in the explosion-proof valve gear for nonaqueous electrolyte cells of this invention, The obturation board which obturated opening of the aforementioned case and welded the resin film for explosion-proof valves, The up insulating gasket which insulates the rivet which serves as the terminal inserted in the center section of the obturation board, and an obturation board and a rivet, It has the metal washer which connects electrically a rivet and the lead board of the like-pole nature of a group of electrode through the lower insulating gasket of a rivet. a case and an obturation board What could weld by laser welding and prepared the pouring-in mouth in the obturation board, That to which the periphery section of an obturation board was cratered in the concave, what has a circular hole for explosion-proof valves, The thing made to deform the hole upper surface for explosion-proof valves so that it may have the needlelike height which projects in the direction of a center of the hole for explosion-proof valves on the upper surface of the hole for explosion-proof valves, Or the thing which is welding the metal plate which has a needlelike lobe in the direction of an inferior surface of tongue of the hole for explosion-proof valves to the upper surface of the hole for explosion-proof valves, Moreover, that by which the lower part of the hole for explosion-proof valves of the cover plate of an obturation board or the whole inferior surface of tongue of a cover plate is welded by a wrap or ultrasonic welding in the aluminum foil with the aluminum foil can be made into an operation gestalt.

[0015]

[Example] Hereafter, the concrete example of this invention is explained, referring to a drawing.

[0016] Drawing 1 is an example equipped with the explosion-proof valve gear for nonaqueous electrolyte cells of this invention of the cross section of a cell. 1 is the case of the square shape made from aluminum. 2 is an obturation board and the explosion-proof valve 3 is formed in plate-like cover-plate 2a made from aluminum. And the explosion-proof valve 3 is covered by resin film 2b of the product [ inferior surface of tongue / of the hole 4 for explosion-proof valves of cover-plate 2a ] made from polypropylene. Laser welding of this obturation board 2 is carried out to the case 1 of a square shape. The rivet which 5 served as the iron terminal by which nickel plating was carried out, and was arranged in the center section of the obturation board 2, the up insulating gasket from which 6 insulates a rivet 5 with the obturation board 2, the iron washer with which nickel plating of 7 was carried out, and 8 are lower insulating gaskets which insulate a washer 7 with the obturation board 2. After inserting this rivet 5 in opening of the center section of the obturation board 2 through the up insulating gasket 6 and arranging a washer 7 in the lower part of a rivet 5 through the lower insulating gasket 8, while taking the electrical installation of a rivet 5 and a washer 7 by closing a rivet 5, the insulation with cover-plate 2a is also secured. 9 is the pouring-in mouth which was able to be opened in cover-plate 2a, and 10 is a plug which closes the pouring-in mouth 9. 11 is the group of electrode by which press compression was carried out through separator at winding and the ellipse in the positive-electrode board and the negative-electrode board. 12 is welded to cover-plate 2a with the lead for positive-electrode current collection made from aluminum taken out from the positive-electrode board. Moreover, 13 is welded to the washer 7 with the lead for negative-electrode current collection made from nickel taken out from the negative-electrode board. Therefore, the terminal with which a case 1 is a positive electrode and consists of a rivet 5 as a cell serves as a negative electrode. And with this obturation board 2, when the cell internal pressure by accumulation of the gas in the cell at the time of unusual use of the short circuit of a cell, overcharge, reverse charge, etc. rises, resin film 2b of the polypropylene of the hole 4 for explosion-proof valves prepared in the obturation board 2 is fractured, and it becomes possible by discharging the gas in a cell to prevent rapid elevation of cell internal pressure.

[0017] The cell equipped with the explosion-proof valve gear for nonaqueous electrolyte cells of this invention was produced as follows. A positive-electrode board is LiCoO<sub>2</sub> which is an active material. After having plastered both sides of an aluminum foil with what was mixed the aqueous dispersion of polytetrafluoroethylene by the weight ratio of a solid content as an electric conduction agent, and was mixed at a rate of 100:3:10 as a binder, drying and rolling out carbon black, it cut in the predetermined size. The lead board for positive-electrode current collection made from aluminum is welded to this. The negative-electrode board made carbonaceous material the main material, and after plastering both sides of copper foil with

what was mixed at a rate of 100:5 by the weight ratio, drying and rolling out this and a styrene-butadiene-rubber system binder, it cut it in the predetermined size. The lead for negative-electrode current collection made from nickel is welded to this. Separator is a fine porosity film made from polyethylene. Winding and the upper surface make a positive-electrode board and a negative-electrode board the group of electrode of an ellipse through separator.

[0018] The lead 13 for plate current collection is welded to the obturation board 2, it inserts in the case 1 of a square shape, and the obturation board 2 and a case 1 are obturated by laser welding. As shown in drawing 1, laser spot welding of the lead 12 for positive-electrode current collection was carried out to cover-plate 2a of the obturation board 2 made from aluminum, and the lead 13 for negative-electrode current collection was welded by resistance to the iron washer 7 by which nickel plating was carried out. Next, it carries out specified quantity pouring in of the electrolytic solution from the pouring-in mouth 9. In this example, the pipe with which the ring made of rubber is attached at the nose of cam of the pouring-in mouth 9 is inserted. As for the pipe, it has the method cock of three, and one side is connected [ another side ] to the pump into which the electrolytic solution went at the vacuum pump for one side at the cell.

[0019] The inside of a cell is lengthened to reduced pressure with a vacuum pump through a pipe. Next, clysis was performed by the method of changing a cock and pouring in the electrolytic solution from a pump. Pouring of the electrolytic solution becomes easy by lengthening the inside of a cell to reduced pressure at once. What dissolved the 6 fluoride [ phosphoric-acid ] lithium in the solvent which mixed ethylene carbonate and diethyl carbonate by the mole ratio 1:3 by the concentration of one mol/l. as a solute was used for the electrolytic solution.

[0020] (Example 1) The lower insulating gasket 8 which insulates a washer 7 with the up insulating gasket 6 which insulates a rivet 5 with the obturation board 2, and the obturation board 2 is explained. Generally as a resin material, polypropylene resin is used by the nonaqueous electrolyte cell. This resin has the technical problem in elevated-temperature thermal resistance, although a moldability is good and cost is also widely used with the coin type lithium cell etc. the low sake. In order to carry out laser welding of the obturation board 2 of this invention to a case 1 in the laser-welding section 14, we are anxious about the thermal effect to a resin, and to be a thermal comparatively stable resin is desired. The existing data, such as organic-solvent-proof nature and thermal resistance, were narrowed down to reference at four kinds, polypropylene (henceforth PP), a perfluoro-alkoxy fluororesin (henceforth PFA), polysulphone resin (henceforth PS), and a polyphenylene-sulfide resin (henceforth PPS), and this example estimated combining each to the up insulating gasket 6 and the lower insulating gasket 8. The obturation board 2 and the cell were produced using these resins, and the resin was selected by performing the cell liquid spill examination at the time of elevated-temperature preservation. The rate of a liquid spill of each cell (every n= 100 cell) was shown in Table 1. In addition, after saving a liquid spill test method at -50 degrees C for 1 hour, it counted the number of the cell liquid spill articles after 1000 cycles by making into 1 cycle the process saved at 100 degrees C for 1 hour.

[0021]

[Table 1]

樹脂材料		漏液率 (%)
上部絶縁ガスケット	下部絶縁ガスケット	
PP	PP	70%
PFA	PP	10%
PP	PPS	40%
PFA	PFA	0%
PS	PS	0%
PPS	PPS	0%
PFA	PPS	0%
PPS	PS	0%
PS	PFA	0%

[0022] Liquid spill-proof nature improves by leaps and bounds by using PFA, PS, and PPS to PP currently used conventionally in an obturation plate structure like this invention, as shown in Table 1. Moreover, even if it combines PFA, PS, and PPS arbitrarily in addition to table 1, liquid spill-proof nature is securable.

[0023] (Example 2) The advantage which forms the needlelike height 15 in the upper surface of the hole 4 for explosion-proof valves of the obturation board 2 in the direction of an inferior surface of tongue of a hole is explained. In this invention, the hole 4 for explosion-proof valves is formed in cover-plate 2a of the obturation board 2, and although the wrap explosion protection valve structure is carried out by PP film, when cell internal pressure rises unusually and the explosion-proof valve 3 operates, PP film swells up and fractures the inferior surface of tongue after that. Therefore, a valve working pressure is greatly influenced with the thickness of PP film, the configuration of the hole 4 for explosion-proof valves, etc.

[0024] In this invention, as shown in drawing 2, on the upper surface of the hole 4 for explosion-proof valves, by welding the metal plate 16 which has the needlelike height 15 in the direction of an inferior surface of tongue of the aforementioned hole 4 for explosion-proof valves, the fracture position of the explosion-proof valve 3 can be limited at the time of an explosion-proof valve action, and stabilization of a working pressure can be attained. Variation in the working pressure in the case where it does not prepare with the case where the needlelike height 15 is formed in the upper surface of such a hole 4 for explosion-proof valves was compared. The result was shown in Table 2.

[0025]

[Table 2]

針状突起部の有無	弁作動圧平均[kgf/cm <sup>2</sup> ]	バラツキ[σ]
有り	9.8	0.4
無し	10.1	0.9

[0026] The way in which the needlelike height 15 was formed so that more clearly than Table 2 is stabilized by variation few. Moreover, although the metal plate 16 which has the needlelike height 15 was welded in this example, as shown in drawing 3, a part of cover-plate 2a upper surface of the obturation board 2 may be made to deform, and the needlelike height 15 may be formed.

[0027] (Example 3) The valve working pressure of the explosion-proof valve 3 of the obturation board 2 is explained using drawing 4. At the time of the usual cell use, the explosion-proof valve 3 has the sealing nature of a cell, and at the time of rapid elevation of the cell internal pressure at the time of unusual use of a cell, in order [ the ] to carry out a valve action certainly and to emit the gas in a cell outside, it needs to set up a proper working pressure. The valve working pressure was evaluated in this example, using PP film and aluminum foil 2c which carried out ultrasonic welding as an explosion-proof valve 3. Moreover, the cell equipped with the aforementioned explosion-proof valve 3 was produced, and the cell liquid spill examination and the overcharge safety assessment were performed. The evaluation result of a valve working pressure was shown in Table 3, and the cell liquid spill examination and overcharge safe sex-test result was shown in Table 4. In addition, after saving a liquid spill test method at -50 degrees C for 1 hour, it counted the number of the cell liquid spill articles after 1000 cycles by making into 1 cycle the process saved at 100 degrees C for 1 hour. Moreover, the overcharge safe sex-test method checked the existence of the cell ignition when doing non-controlled 2C charge of the cell of a full charge state further.

[0028]

[Table 3]



		弁作動圧平均[kgf/cm <sup>2</sup> ]	バラスキ[σ]
PP膜 (膜厚み)	8 μm	1.2	1.1
	10 μm	3.7	0.5
	60 μm	9.8	0.4
	100 μm	13.5	0.4
	120 μm	20.7	0.8
アルミニウム箔膜 (膜厚み)	8 μm	1.0	1.0
	10 μm	3.0	0.3
	40 μm	13.1	0.4
	50 μm	17.3	1.9

[0029]

[Table 4]

		漏液率(%)	安全性(発火の有無)
PP膜 (膜厚み)	8 μm	45%	発火なし
	10 μm	0%	発火なし
	60 μm	0%	発火なし
	100 μm	0%	発火なし
	120 μm	0%	発火
アルミニウム箔膜 (膜厚み)	8 μm	50%	発火なし
	10 μm	0%	発火なし
	40 μm	0%	発火なし
	50 μm	0%	発火

[0030] By the thickness of 10 micrometers or less, the liquid spill of a cell has generated PP film and the aluminum foil film from Table 4. This is considered to have carried out the valve action by the generation of gas by disassembly of the minute amount moisture in a cell, decomposition of the electrolytic solution, etc. Moreover, by 100 micrometers or more of PP films, and 40 micrometers or more of aluminum foil films, it is thought that the laser-welding section 14 opened wide previously, and ignited rather than the valve action. From the above-mentioned result and Table 3, they are a working pressure 2 - 15 kgf/cm<sup>2</sup>. It is a working pressure with an explosion-proof proper valve.

[0031] Moreover, although PP film and the aluminum foil film were used in this example, a polyethylene-terephthalate resin film, a PFA film, PS film, and a PPS film are sufficient.

[0032] (Example 4) The advantage which is carrying out the configuration which bent in the direction of a group of electrode 11 as the lower insulating gasket 8 of the obturation board 2 showed drawing 1 is explained. In this invention, it is the

structure of arranging a washer 7 through the lower insulating gasket 8, and closing by the rivet 5, and the lead 13 for negative-electrode current collection of a group of electrode 11 is welded to the aforementioned washer 7. Therefore, at the time of the fall shock of a cell, by the case where it falls especially for inversions, a group of electrode 11 may shift to the cell upper part, the lead 13 for riser negative-electrode current collection may bend, it may eat into a group of electrode 11, or a case 1 may be contacted, and internal short-circuit may be caused. By arranging the lower insulating gasket 8 between a group of electrode 11 and the obturation board 2 to it, a group of electrode 11 shifts, a riser is suppressed, and it is thought that the safety of a cell is securable.

[0033] In this invention, in the time of a fall shock etc., the plate shifted by carrying out the configuration which bent in the direction of a group of electrode 11 so that the metal washer 7 which the lower insulating gasket 8 connects with the lead 13 for negative-electrode current collection of a plate electrically as shown in drawing 1 might be surrounded, and the riser is suppressed. The fall impact test of a cell was performed by the case where it does not prepare with the case where the bending section of such a lower insulating gasket 8 is prepared, and the result was shown in Table 5. In addition, the fall impact test method of a cell counted the internal short occurrences of the cell when making a cell upside-down and falling 20 times on concrete from a height of 1m.

[0034]

[Table 5]

下部絶縁ガスケット 折れ曲がり部の有無	内部ショート発生率(%)
有り	0%
無し	60%

[0035] The way in which the bending section of a lower insulating gasket was prepared so that more clearly than Table 5 can improve the reliability of a cell.

[0036]

[Effect of the Invention] According to this invention, the explosion-proof valve gear for nonaqueous electrolyte cells which has the high safety which could discharge gas with a sufficient precision to elevation of the cell internal pressure in misuse, the unusual situations, etc. of a cell, such as a short circuit, overcharge, and reverse charge, and was excellent in liquid spill-proof nature, and reliability can be offered as mentioned above.

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[Translation done.]

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2. \*\*\*\* shows the word which can not be translated.
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CLAIMS

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[Claim(s)]

[Claim 1] A group of electrode, the case where the electrolytic solution is held in the interior, and the obturation board that obturated opening of the aforementioned case and was equipped with the explosion-proof valve, The up insulating gasket made of a resin which insulates the rivet which serves as the terminal arranged by the aforementioned obturation board, and the aforementioned obturation board and the aforementioned rivet, The lower part of the aforementioned rivet is equipped with the metal washer which connects electrically the aforementioned rivet and the lead board of like-pole nature through the lower insulating gasket made of a resin. the aforementioned obturation board The explosion-proof valve gear for nonaqueous electrolyte cells constituted by preparing the hole for explosion-proof valves in the cover plate, and covering the lower part of the aforementioned hole for explosion-proof valves by the resin film.

[Claim 2] An up insulating gasket is an explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 which is the quality of the material chosen from a perfluoro-alkoxy fluororesin, polysulphone resin, and the polyphenylene-sulfide resin.

[Claim 3] A lower insulating gasket is an explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 which is the quality of the material chosen from a perfluoro-alkoxy fluororesin, polysulphone resin, and the polyphenylene-sulfide resin.

[Claim 4] A lower insulating gasket is an explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 which is carrying out the configuration which bent in the direction of a group of electrode so that the metal washer electrically connected with the lead for current collection of a group of electrode might be surrounded.

[Claim 5] The resin film arranged by the lower part of the hole for explosion-proof valves is an explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 which is one kind of quality of the material chosen from a polyethylene-terephthalate resin, a perfluoro-alkoxy fluororesin, polysulphone resin, and the polyphenylene-sulfide resin.

[Claim 6] It consists of thickness of 10-100 micrometers, and the resin film arranged by the lower part of the hole for explosion-proof valves is 2 - 15 kgf/cm<sup>2</sup>. Explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 fractured by pressurization.

[Claim 7] It is constituted by the explosion-proof valve of an obturation board wearing only the lower part of the hole for explosion-proof valves prepared in the cover plate with an aluminum foil, and wearing the whole inferior surface of tongue of a wrap or a cover plate with an aluminum foil, the aforementioned aluminum foil consists of thickness of 10-40 micrometers, and it is 2 - 15 kgf/cm<sup>2</sup>. Explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 fractured by pressurization.

[Claim 8] It is constituted by wearing with an aluminum foil in ultrasonic welding, and wearing the whole inferior surface of tongue of a wrap or a cover plate only for the lower part of the hole for explosion-proof valves by which the explosion-proof valve of an obturation board was prepared in the cover plate with an aluminum foil in ultrasonic welding, the aforementioned aluminum foil consists of thickness of 10-40 micrometers, and it is 2 - 15 kgf/cm<sup>2</sup>. Explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 fractured by pressurization.

[Claim 9] The explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 made to deform the hole upper surface for explosion-proof valves into the upper surface of the hole for explosion-proof valves of an obturation board so that it may have the needlelike height which projects in the direction of a center of the aforementioned hole for explosion-proof valves.

[Claim 10] The explosion-proof valve gear for nonaqueous electrolyte cells according to claim 1 which welded the metal plate which has a needlelike height in the direction of an inferior surface of tongue of the aforementioned hole for explosion-proof valves to the upper surface of the hole for explosion-proof valves of an obturation board.

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[Translation done.]